Initiator Effects in Reactive Extrusion of Starch–Polyacrylamide Graft Copolymers

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ABSTRACT: Starch–polyacrylamide (PAAm) graft copolymers were prepared by reactive extrusion using ammonium persulfate (APS), ceric ammonium nitrate (CAN), or ferrous ammonium sulfate/hydrogen peroxide (FAS/H_2O_2) as initiator. The initiator contents, measured as anhydroglucose units per initiator radical (AGU/I), ranged from 70 to 280 AGU/I for CAN and FAS and 70 to 1140 for APS. CAN was not an effective initiator, giving low conversions, low graft content, low grafting efficiencies, and no detectable high molecular weight PAAm. FAS/H_2O_2 gave conversions of approximately 80%, graft efficiencies of approximately 50%, and PAAm molecular weights from 75,000 to 357,000, depending on the initiator content and starch/AAm ratio. APS gave conversions exceeding 90% with graft efficiencies of approximately 75%. PAAm molecular weights with APS were 575,000 and higher. As the AGU/I ratio increased above 280 for APS, the conversion and graft content decreased whereas the graft efficiency was essentially constant. Initiation with APS gave fewer PAAm grafts of higher molecular weight compared to FAS/H_2O_2. © 2005 Wiley Periodicals, Inc.* J Appl Polym Sci 99: 52–58, 2006

Key words: starch; polyacrylamide; graft copolymers; reactive extrusion; biopolymers; water-soluble polymers

INTRODUCTION

Starch graft copolymers have been investigated for many years.[1,2] Although various types of initiators have been used, considerable work has focused on ceric ammonium nitrate (CAN). CAN forms complexes with hydroxyl groups on glucose rings; subsequent disproportionation of this complex generates free radicals on the starch molecule that can initiate polymerization of unsaturated monomers.[3] Other free-radical initiators, including persulfate salts or redox pairs such as ferrous salts/H_2O_2 (Fenton's reagent), rely on hydrogen abstraction to generate free radicals on the starch and often yield significant amounts of ungrafted homopolymer. Starch graft copolymers are commonly prepared in aqueous slurries with approximately 20% solids, because the graft copolymer can be isolated by filtration rather than precipitation. This process has limited utility when using water-soluble monomers because of the formation of significant amounts of ungrafted homopolymer.[2]

Various preparations of starch–polyacrylamide (PAAm) graft copolymers using batch processes were reported.[4–11] The initiators that were used include CAN,[4–9] Fenton's reagent,[5] potassium persulfate,[10] and KMnO$_4$/citric acid,[11] which cover a wide range of AAm/starch ratios, initiator concentrations, and reaction times. The grafting efficiencies were generally less than 50%, and reaction times up to 24 h were required for high conversions. In the few cases where PAAm molecular weights are reported, they were less than 100,000.[5,6]

Another route to prepare graft copolymers is reactive extrusion. The advantages of reaction extrusion for modification of starch include reduced water use (higher solids), the ability to continuously process high-viscosity materials, and short reaction times. Carr et al. prepared starch–PAAm graft copolymers using CAN as an initiator,[12] and their anhydroglucose unit (AGU)/CAN ratios ranged from 45 to 230. Conversion of AAm decreased from 30 to 12% with decreasing starch/AAm ratios. At a starch/AAm feed ratio of 1:1, the graft content was 16%. No molecular weight or graft efficiency data were given. We recently reported the preparation of starch–PAAm graft copolymers with monomer conversions exceeding 80% and grafting efficiencies up to 80.5%, using ammonium persulfate (APS) as the initiator at an AGU/sulfate radical ratio of 70.[13] PAAm molecular weights up to

527,000 were obtained, depending on the extrusion parameters such as the feed rate, starch/AAm ratio, and screw speed. However, little is known about the differences between free-radical initiators in the reactive extrusion of starch graft copolymers. To investigate the effects of various initiators, we prepared starch–PAAm copolymers using three initiators: CAN [$(NH_4)_2Ce(NO_3)_6$], APS [$(NH_4)_2S_2O_8$], and ferrous ammonium sulfate/hydrogen peroxide [FAS, $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$], which is Fenton's reagent. The effects of the initiator content and monomer content on the monomer conversion, graft content and efficiency, graft molecular weight, and graft frequency are reported.

EXPERIMENTAL

Materials

An unmodified corn starch (Pure Food Powder, Tate & Lyle, Decatur, IL) was used for all extrusion runs. Prior to extrusion, the starch (moisture content ≈10%) was sifted through a 20-mesh screen to remove lumps and deoxygenated by flushing with nitrogen at 100 kPa. APS, CAN, FAS (hexahydrate, Sigma–Aldrich), and hydrogen peroxide (30% aqueous solution, Fisher) were used as received. In-house deionized water was sparged overnight with helium to remove dissolved oxygen. AAm monomer (Cytec, Inc.) was supplied as a 50 wt % solution and used as received. FAS and H_2O_2 (diluted to 1%) were used at a 1 : 1 molar ratio.

Extrusion

The extruder was a Werner Pfleiderer ZSK30 corotating twin-screw extruder (Coperion, Ramsey, NJ) with 14 barrel sections (length/diameter ratio = 44), including the feed section. The screw configuration is described elsewhere.[13] Starch (ambient moisture) was fed using a weight-loss feeder (AccuRate Inc., Whitewater, WI) at a rate of 75 g/min (67.5 g/min solids) for all runs. During extrusion, the feed hopper, nozzle, and feed throat were enclosed and continuously purged with nitrogen. The moisture content for all runs was fixed at 50%. Water and initiator solution were pumped into barrel section 2, and initiator solution was also injected into barrel section 8. FAS and H_2O_2 solutions were fed separately, and FAS was injected before H_2O_2. Initiator levels were chosen to give molar ratios of AGU to initiator (I) of approximately 70, 140, and 280. With APS, the AGU/I range was expanded to 1140. Monomer solution was injected into barrel section 4. All liquids were metered by separate triple piston pumps (model BBB-4, Eldex Laboratories, Napa, CA). Samples of extrudates were taken at the die (twin 4-mm holes). After each change

in processing parameters, the extruder was run for approximately 3 retention times before sampling. Variations in feed rates and pump rates were approximately ±3% of the desired set points.

Initiator solutions were prepared immediately prior to extrusion. Although pH affects the complexation equilibrium between CAN and AGUs,[14] CAN solutions were used as prepared and the pH was not adjusted. Carr et al. showed that the pH had no significant effect on the conversion of AAm when fresh CAN solutions were used in reactive extrusion.[12] In addition, the low pH levels often used with CAN (pH ≈2) can be corrosive and cause extensive hydrolysis of the starch.

The feed throat (barrel section 1) was cooled with 5°C water. The remaining sections were divided into five dual section zones (2–3, 4–5, 6–7, 9–10, 11–12) and three single section zones (8, 13, 14). Barrel temperatures for all runs were 80 (sections 2–3), 90 (sections 4–5, 6–7, 8), 110 (sections 9–10, 11–12), 100 (section 13), and 80°C (section 14).

Extrudate samples (≈50 g, collected for ≈15 s) were immediately placed in 200 mL of ethanol with 0.5 wt % hydroquinone and ground for 4 min in a Waring blender to quench the reaction. The ground extrudates were steeped overnight in the hydroquinone solution to remove unreacted monomer. (PAAm is insoluble in ethanol.) The extrudates were then filtered, washed with ethanol, and dried.

Characterization

Dry extrudates were analyzed for nitrogen content (wt % N) using a Perkin–Elmer 2400 Series II Dumas-type H/C/N analyzer. Monomer conversion was determined by the ratio of the nitrogen content (wt % N) in the quenched extrudate to the nitrogen content in the feed (calculated using measured feed rates). Homopolymer PAAm was extracted by stirring overnight at room temperature in a water/ethanol solvent (70/30 w/w). Graft content and graft efficiencies were calculated based on the nitrogen content after extraction.[13]

Graft frequency is a measure of the average spacing, in terms of AGUs between graft sites. A convenient measure of graft frequency is the number of AGUs per graft (N_{AGU}), which is defined as

$$N_{AGU} = \frac{M_W}{2M_{AGU}} \frac{(1 - g)}{g}$$

where M_w is the weight-average molecular weight as measured by gel permeation chromatography (GPC), M_{AGU} is the AGU molecular weight (162 g/mol), and g is the graft content measured after extraction of homopolymer PAAm.[13]

TABLE I
Properties of Starch–Polyacrylamide Copolymers Prepared Using CAN

Starch/AAm ratio	AGU/initiator ratio	Conversion (%)	Graft content (%)	Graft efficiency (%)
3 : 1	280	15.2	1.0	24.3
3 : 1	140	10.8	1.1	20.5
3 : 1	70	11.2	1.7	17.4
2 : 1	70	—	—	—
1.6 : 1	70	—	—	—
1.3 : 1	70	15.6	2.5	24.0
1.3 : 1	280	7.2	1.0	20.7

(—)Not determined.

Prior to the determination of the molecular weight by GPC, starch was removed by enzyme hydrolysis. Approximately 100 mg of copolymer were dispersed in 100 mL of hot distilled water. Pullulanase and α-amylase (Megazyme) were added in excess, and the mixture (pH 6) was digested overnight with gentle agitation. Completion of starch hydrolysis was confirmed by thin layer chromatography and Lugol iodine.

Molecular weights were determined by GPC using Shodex 804 and 806 columns in series. The flow rate of the mobile phase (0.1M NaNO$_3$) was 0.8 mL/min with a column temperature of 45°C. Aliquots of the starch digestions were injected without further purification. PAAms (Polysciences) were used as standards. Data acquisition and analysis were performed using ChromQuest and Polymer Labs GPC RE analysis software, respectively.

RESULTS AND DISCUSSION

Controls with no initiator

To provide baseline data for the performance of the initiators, control runs with no initiator were conducted with a starch/AAm ratio of 3 : 1. Average conversion for the control runs was 10.5% ($\pm$2.5%), indicating that limited polymerization occurs in the absence of initiator. Limited grafting occurs in the absence of initiator, because the average graft content was 0.6% ($\pm$0.4%). Graft efficiencies showed considerable variation, with an average value of 20.5% ($\pm$13.8%). Given the low conversions and graft contents, the differences in graft efficiency are not significant and reflect the variation in experimental results. The graft efficiency results show that a limited amount of grafting occurs, presumably through chain transfer to starch. The molecular weights of grafted PAAm were not determined for the control samples.

CAN initiator

Consistent with the results of Carr et al.,[12] conversion levels with CAN were approximately 15% or less, as shown in Table I. The conversion levels are not appreciably higher than control levels, indicating that CAN is not a suitable initiator for AAm in reactive extrusion. Grafting efficiencies with CAN are relatively low (21.4 $\pm$ 2.8%) and are comparable to those observed in slurry polymerizations with starch.[4,5] Graft yields with CAN reflect the low conversion levels seen in Table I. Although grafting efficiencies with CAN are less than that of the control, it is noted that the low conversion and low grafting levels of the control introduce large uncertainty in the measured efficiencies. CAN yielded low molecular weight PAAm, which eluted from the GPC columns with a retention time comparable to the lowest molecular weight PAAm standard (22,000). CAN-initiated aqueous polymerization of AAm is known to yield low molecular weight PAAm because of oxidative termination of polymer radicals by CAN.[5,15,16] Any higher molecular weight PAAm in the CAN-initiated samples was present in amounts below the detection limit of GPC and is of little interest, given the low conversions and grafting levels obtained with CAN. Grafting frequencies (N_{AGU}) were not calculated, considering the low conversion and graft content in these copolymers.

TABLE II
Properties of Starch–Polyacrylamide Copolymers Prepared Using FAS/H$_2$O$_2$

Starch/AAm (weight ratio)	AGU/initiator (molar ratio)	Conversion (%)	Graft content (%)	Graft efficiency (%)	Graft molecular weight ($\times 10^{-3}$)	Graft frequency N_{AGU}	Graft sites/ initiator (g/l)
3 : 1	280	82.4	14.6	58.6	133	2400	0.117
3 : 1	140	85.0	14.2	53.0	86	1600	0.087
3 : 1	70	83.5	14.0	51.4	75	1400	0.050
2 : 1	70	91.6	18.3	46.6	118	1600	0.044
1.6 : 1	70	93.2	21.5	43.1	149	1700	0.041
1.3 : 1	70	85.2	23.3	46.9	193	2000	0.035
1.3 : 1	280	86.1	24.6	49.5	357	3300	0.085

FAS/H$_2$O$_2$ initiator

Results for reactive extrusion with FAS/H$_2$O$_2$ are shown in Table II. Conversions ranged from 82.4 to 93.2% and did not show a consistent dependence on either monomer or initiator content over the range that was studied. Graft contents are essentially independent of the initiator content at a fixed starch/AAm ratio, and they steadily increase with increasing monomer content. The average grafting efficiency was 49.9% (±5.1%). Graft molecular weights ranged from 75,000 to 357,000 g/mol and increased as either monomer content increased or initiator content decreased, which is consistent with free-radical polymerization kinetics.[17] The PAAm molecular weights in Table II are significantly higher than those reported by Fanta et al.,[5] although the AGU/FAS ratios here are 4–10 times lower. The larger molecular weights obtained by reactive extrusion compared to slurry polymerization may reflect the higher monomer concentration during extrusion at 50% moisture content, compared to the slurry process. At constant monomer content, N_{AGU} increases with decreasing initiator content. This result is in general agreement with free-radical chain transfer kinetics, wherein the rate of chain transfer increases with initiator concentration.[17] Assuming that N_{AGU} varies inversely with the rate of chain transfer, N_{AGU} should increase with decreasing initiator concentration, as seen in Table II. This argument also predicts an inverse relationship between N_{AGU} and the monomer concentration, but Table II shows an increase in N_{AGU} with increasing monomer content. This discrepancy may be related to chain termination of AAm polymerization by ferric ions.[18,19]

For comparison, a control run using a 3 : 1 starch/AAm ratio was conducted in which the FAS was omitted and only H$_2$O$_2$ injected at a level of 70 AGU/initiator. Conversion (50.7%) and graft content (7.2%) were approximately half the values obtained when FAS was present, whereas the grafting efficiency (51.3%) was comparable to that in the presence of FAS. The PAAm molecular weight was significantly greater (237,000) and the N_{AGU} increased from 1400 to 9500. The reduction in conversion is consistent with the well-known catalytic ability of ferrous salts to generate free radicals by reaction with hydrogen peroxide; in other words, conversion is lower because of the slower reaction of H$_2$O$_2$ in the absence of FAS. The significant increase in molecular weight reflects the absence of ferric ions produced by the reaction of FAS with H$_2$O$_2$. The increase in N_{AGU} indicates that fewer grafting sites are introduced on the starch in the absence of FAS. A possible explanation for this effect is that the effective initiator concentration is reduced because of the slower decomposition kinetics of H$_2$O$_2$; as mentioned above, a lower initiator concentration leads to a higher N_{AGU}.
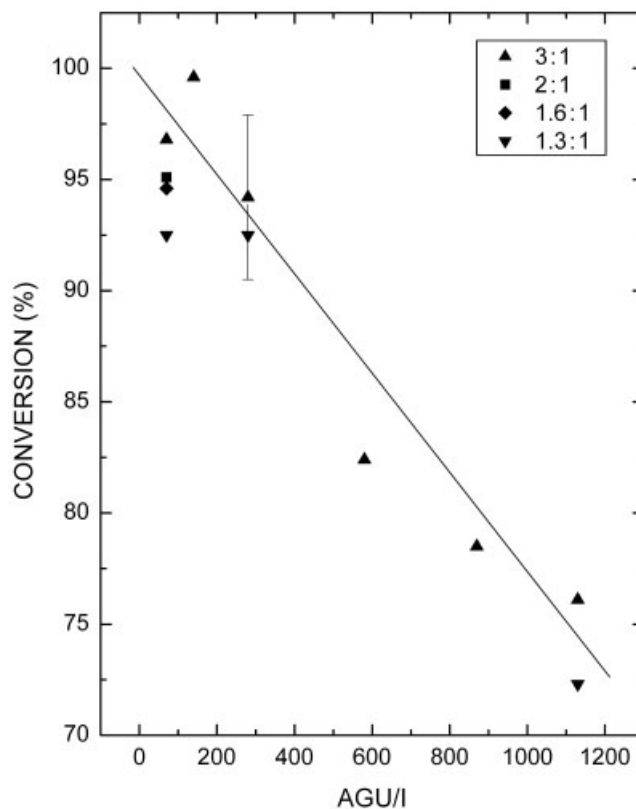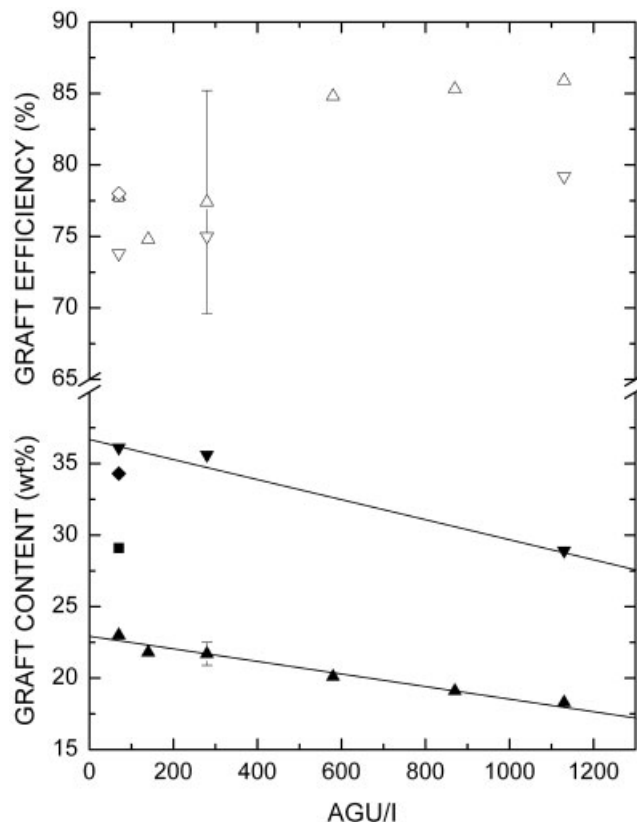

Figure 1 The effect of the ammonium persulfate content, expressed as anhydroglucose units per initiator radical (AGU/I), on the conversion. Starch/acrylamide ratios are (▲) 3 : 1, (■) 2 : 1, (♦) 1.6 : 1, and (▼) 1.3 : 1. Error bars are for duplicate runs with starch/acrylamide = 3 : 1 and AGU/I = 280. A line is drawn to guide the eye.

Another parameter of interest is the ratio of graft sites to initiator molecules (g/I), which is the ratio of the initiator content (AGU/I) to N_{AGU}. As seen in Table II, this ratio increases as the FAS/H$_2$O$_2$ content decreases. The FAS/H$_2$O$_2$ system is more effective at introducing graft sites on the starch as the initiator concentration decreases. In contrast, increasing the monomer content decreases this ratio. The g/I ratio decreases by an order of magnitude (from 0.050 to 0.007) when FAS is omitted.

APS initiator

The APS content ranged from 70 to 1140 AGU/initiator radical (2 radicals/APS molecule). Duplicate runs with a starch/AAm ratio of 3 : 1 and AGU/I of 280 were made; variations in the data between the two runs are indicated by the error bars in Figures 1–6. As shown in Figure 1, conversions exceeded 90% for AGU/I ratios of 280 or less for all starch/AAm ratios. These conversion levels are significantly greater than those obtained with CAN and FAS/H$_2$O$_2$. Conversion decreased to less than 80% at the lowest APS level
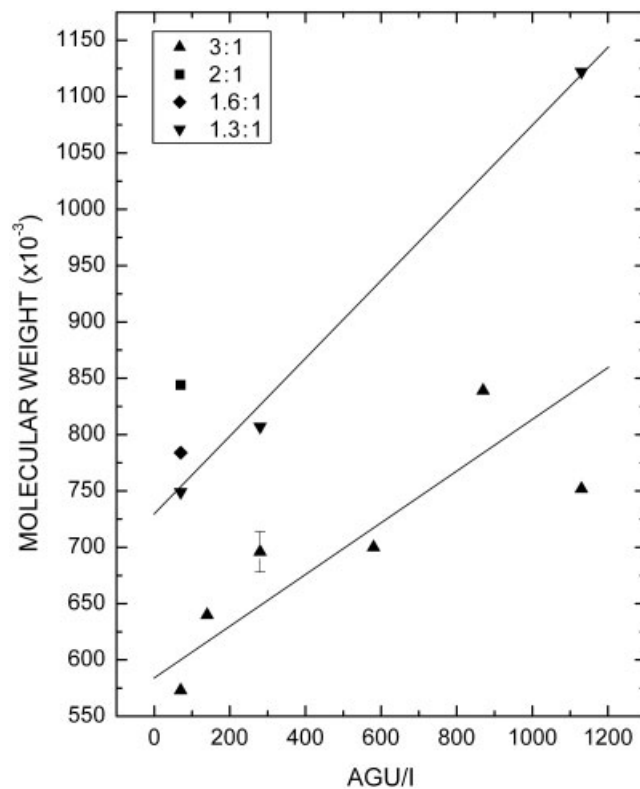
Figure 2 The effect of the ammonium persulfate content, expressed as anhydroglucose units per initiator radical (AGU/I), on the graft content and graft efficiency. Starch/acrylamide ratios are ($\triangle$, $\blacktriangle$) 3 : 1, ($\square$, $\blacksquare$) 2 : 1, ($\diamond$, $\blacklozenge$) 1.6 : 1, and ($\triangledown$, $\blacktriangledown$) 1.3 : 1; filled symbols are graft content, and open symbols are graft efficiency. Error bars are for duplicate runs with starch/acrylamide = 3 : 1 and AGU/I = 280. Lines are drawn to guide the eye.

used. It was essentially independent of the monomer content at AGU/I ratios of 70, 280, and 1140. The graft contents are shown in Figure 2. APS gave higher graft contents at an equivalent starch/AAm ratio than CAN and FAS/H$_2$O$_2$. At a fixed starch/AAm ratio, the graft content gradually decreased with decreasing initiator content whereas the graft efficiency was essentially independent of the APS content (Fig. 2). At a starch/AAm ratio of 3 : 1, the graft content is directly proportional to the conversion (r^2 = 0.99, data not shown), suggesting that the reduction in graft content (as AGU/I increases) is correlated with reduced conversion of monomer to polymer. The graft contents and efficiencies shown in Figures 1 and 2 are consistent with our previous results using this initiator.[13]

The molecular weights of grafted PAAm obtained with APS are shown in Figure 3. APS yields a PAAm with significantly higher molecular weight than FAS/H$_2$O$_2$ and CAN. The PAAm molecular weight increased with decreasing APS content, consistent with free-radical polymerization kinetics. Increasing the monomer content also increased the PAAm molecular

weight, as expected. The higher molecular weights obtained with APS are partly attributable to the absence of Ce^{4+} and Fe^{3+} ions, which are effective polymerization terminators. Relative changes in the molecular weight with the initiator or monomer content were less than those observed with FAS/H$_2$O$_2$.

The N_{AGU} values for APS are shown in Figure 4. The values are significantly greater for APS than FAS/H$_2$O$_2$. As seen with FAS/H$_2$O$_2$, N_{AGU} increases steadily as the AGU/I increases, as expected. In other words, lower APS content gave fewer grafts of higher molecular weight. In contrast to FAS/H$_2$O$_2$, however, N_{AGU} decreases as the monomer content increases. This result is in general agreement with chain transfer polymerization kinetics, wherein the rate of chain transfer increases with the monomer content (see above). Because N_{AGU} should vary inversely with the rate of chain transfer, increases in the monomer content should yield lower N_{AGU} values, which was observed. At constant AGU/I, increasing the monomer content gives copolymers with more PAAm grafts of higher molecular weight. Compared to FAS/H$_2$O$_2$, APS yields copolymers with fewer grafts of higher molecular weight.

Figure 3 The correlation between the ammonium persulfate content, expressed as anhydroglucose units per initiator radical (AGU/I), and the weight-average molecular weight of grafted polyacrylamide, after extraction to remove homopolymer and starch hydrolysis. Starch/acrylamide ratios are ($\blacktriangle$) 3 : 1, ($\blacksquare$) 2 : 1, ($\blacklozenge$) 1.6 : 1, and ($\blacktriangledown$) 1.3 : 1. Error bars are for duplicate runs with starch/acrylamide = 3 : 1 and AGU/I = 280. Lines are drawn to guide the eye.
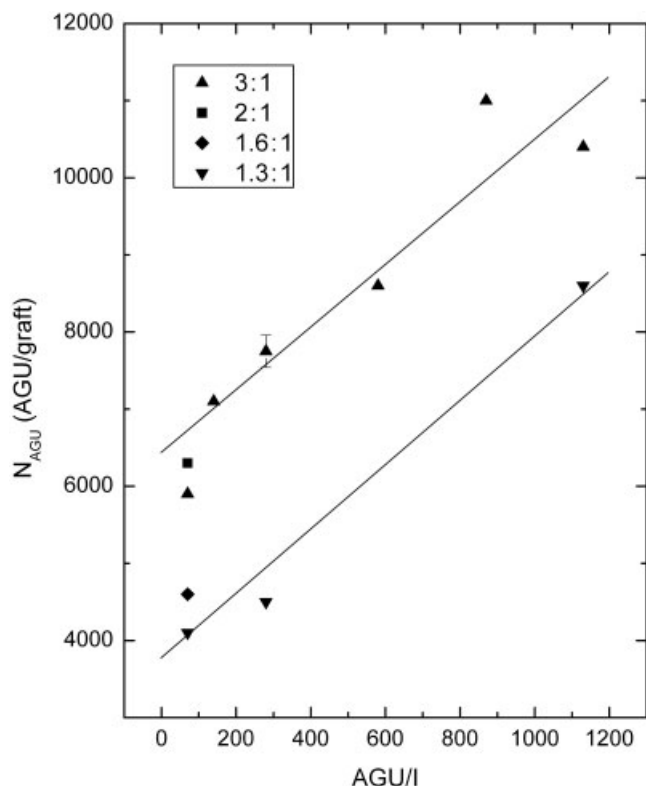
Figure 4 The effect of the ammonium persulfate content, expressed as anhydroglucose units per initiator radical (AGU/I), on the graft frequency. Starch/acrylamide ratios are (▲) 3 : 1, (■) 2 : 1, (♦) 1.6 : 1, and (▼) 1.3 : 1. Error bars are for duplicate runs with starch/acrylamide = 3 : 1 and AGU/I = 280. Lines are drawn to guide the eye.

The g/I ratio is shown in Figure 5 for APS-initiated polymerization. The values are lower than those obtained with FAS/H_2O_2 by a factor of 4 at a starch/AAm ratio of 3 : 1. The ratio increases with decreasing APS concentration (increasing AGU/I). Increasing the monomer content also increases this ratio.

Extrusion parameters

The initiator type had a significant impact on the extrusion parameters. The average die pressure for the controls (no initiator) was 0.19 ($\pm$0.03) MPa. When CAN was used, the die pressures were lower (0.10–0.12 MPa) than the control value, regardless of the initiator content and starch/AAm ratio. FAS/H_2O_2 gave die pressures ranging from 0.52 ($\pm$0.01) to 0.80 ($\pm$0.20) MPa. With APS, the die pressures ranged from 0.97 ($\pm$0.02) to 1.55 ($\pm$0.03) MPa, depending on the total feed rate. At a starch/AAm ratio of 3 : 1, the die pressure was strongly correlated with the extent of conversion, as shown in Figure 6. The error bars represent the variation between two separate runs under these conditions. This increase in die pressure with APS relative to the controls can be attributed in part to

the increased viscosity due to formation of PAAm during extrusion. The greater die pressures are consistent with the higher conversions and PAAm molecular weights obtained with APS.

Similar results are observed for the specific mechanical energy (SME). With no initiator, the average SME was 69 ($\pm$10) kJ/kg. The SME for the CAN runs decreased from 159 (starch/AAm ratio = 3 : 1) to 21 kJ/kg (starch/AAm ratio = 1.3 : 1) and exceeded the control value only for the highest starch/AAm ratio. FAS/H_2O_2 gave SME values ranging from 108 to 273 kJ/kg. The SME values with APS were between 351 and 406 kJ/kg, consistent with the higher conversion and PAAm molecular weights obtained with this initiator.

The die pressures and SME values for the CAN-initiated materials are consistent with the low levels of conversion in Table I, because the presence of unreacted AAm is expected to reduce the viscosity. The low viscosity and syruplike appearance of the extrudates with CAN indicated starch degradation might also be occurring. Soluble fractions from the water/ethanol extractions were analyzed by thin layer chromatography using silica gel plates. After elution, car-
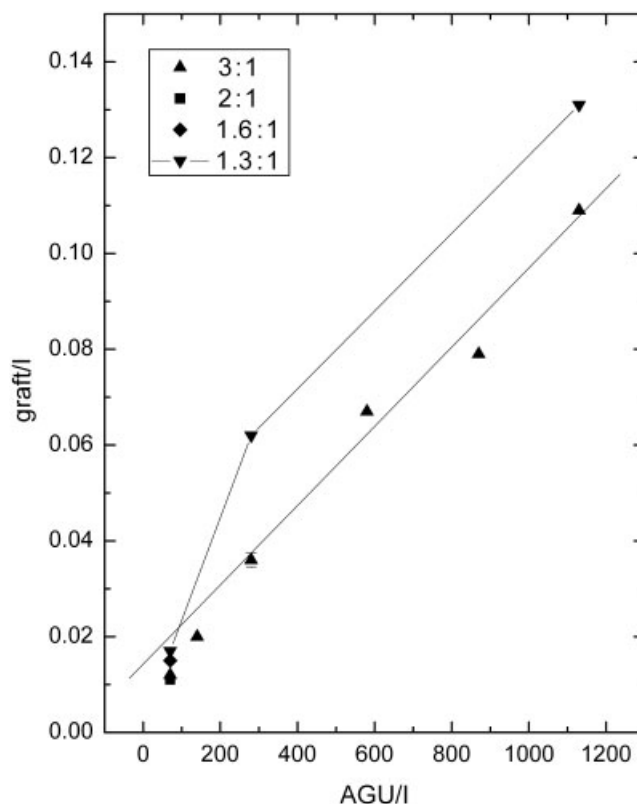
Figure 5 The effect of the ammonium persulfate content, expressed as anhydroglucose units per initiator radical (AGU/I), on the graft/initiator ratio (g/I). Starch/acrylamide ratios are (▲) 3 : 1, (■) 2 : 1, (♦) 1.6 : 1, and (▼) 1.3 : 1. Error bars are for duplicate runs with starch/acrylamide = 3 : 1 and AGU/I = 280. Lines are drawn to guide the eye.
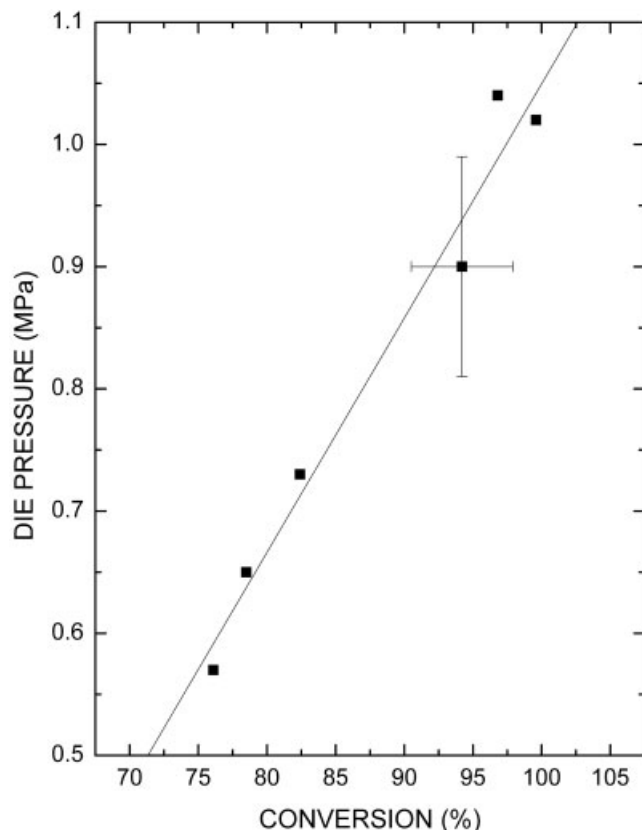
Figure 6 The correlation between die pressure and the degree of conversion with ammonium persulfate; starch/acrylamide = 3 : 1. The line is the least squares fit ($r^2 = 0.97$). Error bars are for duplicate runs with starch/acrylamide = 3:1 and AGU/I = 280.

bohydrates were visualized with *N*-(1-naphthyl)ethyl-enediamine spray reagent. A comparison with a commercial maltodextrin standard (degree of polymerization < 20) showed significant oligomeric carbohydrates in the CAN extrudates, whereas the APS and FAS/H_2O_2 extrudates showed no oligomeric fractions. These results indicate that significant starch hydrolysis occurred during extrusion with CAN.

CONCLUSION

Of the three initiators used in this study, APS gave the highest conversion, graft content, grafting efficiency,

and PAAm molecular weight. CAN was not an effective initiator, giving low conversions and low graft efficiencies, with no detectable high molecular weight PAAm. FAS/H_2O_2 gave conversions of approximately 80% and graft efficiencies of approximately 50%. PAAm molecular weights with FAS/H_2O_2 and APS increased with increasing monomer content and decreasing initiator content, in accord with free-radical polymerization kinetics. APS yielded graft copolymers with fewer PAAm grafts of higher molecular weight than FAS/H_2O_2.

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